Letters to the Editor

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ON THE EVALUATION OF THE COEFFICIENTS OF THERMAL EXPANSION OF CRYSTALS FROM X-RAY DATA

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The purpose of this note is to call attention to some small but vital differences obtained in the methods used in processing X-ray data for the evaluation of the coefficients of thermal expansion. In view of the increased importance of this property of crystalline solids in relation to their structural imperfections, it has become necessary to know, not merely the average values of the coefficient of expansion but also the temperature dependence of the instantaneous values. It is essential, therefore, that the methods used in processing the X-ray data be chosen in a way so as to bring out the correct form of this temperature variation. It is, of course, assumed that the data on cell dimensions are obtained with the highest possible accuracy, taking care to correct all errors, systematic or random.

An important step in this processing is the determination of the derivative (da/dt) at different temperatures. This, with the help of the definition, $\alpha = (1/a_0)(da/dt)$, gives the values of the zero coefficient of expansion at those temperatures. Different methods are in use for the evaluation of this derivative. One of these, used by Wilson (1941), is to obtain the mean value of the derivative over small intervals of temperature by subtracting the experimental values of 'a' and dividing these by the corresponding temperature differences. A variation of this procedure, employed by some workers (Owen and Richards, 1936 and Deshpande and Mudholker, 1960) consists in obtaining the mean values of the derivative from a carefully drawn graph between 'a' and 't'. The values of 'α' are then evaluated for every temperature at which the derivative is found. Least squares treatment of the α-t data, thus obtained, then gives the temperature

dependence of 'α'. This dependence may or may not be linear, a fact which comes out readily from the α-t plot. If the relation is non-linear it is usually expressed in the form given in Eq. (1).

$$\alpha = \alpha_0 + \beta t + \gamma t^2 \qquad \ldots (1)$$

In another method (Stokes and Wilson, 1941 ; Kempter and Elliot, 1959 ; Pathak and Pandya, 1960 and Pathak and Pandya, 1960a) the lattice constant is first expressed as quadratic function of temperature, by the usual method of least squares, giving an expression, as in Eq. (2).

$$a = a_0 + bt + ct^2 \qquad \ldots (2)$$

Differentiation of Eq. (2) with respect to temperature, then, gives the coefficient of expansion as a linear function of temperature as shown in Eq. (3)

$$\alpha = \alpha_0 + \beta t \qquad \ldots (3)$$

This procedure appears to be more rigorous than the first one, but has a serious limitation in as much as the temperature dependence of 'a' comes out necessarily to be linear. This may or may not be its real form. Wilson (1941) has found that this method does not give the best possible representation of the derivative (da/dt), and Stokes and Wilson (1941) have pointed out that in principle, the quadratic function is not satisfactory.

There is thus a fundamental difference between the two methods outlined above. While the first method brings out the non-linear character of the α--t relation, the second one supresses it. This limitation in the second method can be removed if a cubic function in 't' is used instead of Eq. (2). Owen and Williams (1954) have given such an expression for the lattice constant of silver. Similar procedure has also been used by Dheer and Surange (1958) in their macroscopic study on lead. However, this procedure is rarely followed, perhaps because of the larger amount of computational work involved in it.

As a sample case, we have processed the X-ray data on sodium chlorate (Deshpande and Mudholker 1960) by all these method. The results are shown in Fig. 1. Curves I and II represent the results of the first two methods respectively and curve III is obtained by the use of the cubic expression. It is clear from the that there is a close agreement between the curves I and III. Curve II not only suppresses the non-linear variation of 'α' with 't' but, in this particular case, there are significant differences in the values of 'α' at some temperatures. For other substances the values of 'α' given by the three methods may agree with each other, within certain limits, but the possible non-linear nature of α—t curve can not be brought by the second method. The amount of calculations involved in the third method makes it rather lengthy and hence, the first method seems

to offer a practicable procedure for obtaining dependable results on the temperature variation of the coefficient of thermal expansion.

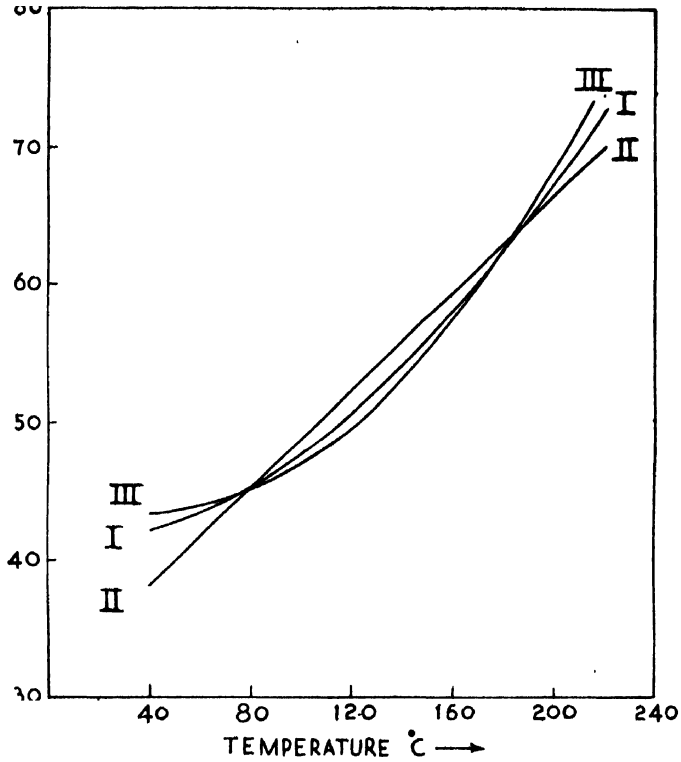

Fig. 1. 'α' vs 't' plots for sodium chlorate as obtained by the three methods of processing X-ray data.

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REFERENCES

Deshpande, V. T. and Mudholker, V. M., 1960, *Acta Cryst.*, **13**, 482.

Dheer, P. N. and Surange, S. L., 1958, Low Temperature Physics and Chemistry, p. 592, Edited by Dillinger, The University of Wisconsin Press.

Kempter, C. P. and Elliot, R. O., 1959, *J. Chem. Phys.*, **30**, 1524.

Owen, E. O. and Richards, T. Ll., 1936, *Phil. Mag.* **22**, 304.

Owen, E. O. and Williams, G. I., 1954, *J. Sci. Instr.*, **31**, 49.

Pathak, P. D. and Pandya, N. V., 1960, *Current Science*, **29**, 14.

Pathak, P. D. and Pandya, N. V., 1960 a, *Ind. J. Phys.* **34**, 416.

Stokes, A. R. and Wilson, A. J. C., 1941, *Proc. Phys. Soc.* **53**, 658.

Wilson, A. J. C., 1941, *Proc. Phys. Soc.* **53**, 235.